

Measurement of electron correlations in Li_xCoO_2 ($x=0.0 - 0.35$) using ^{59}Co nuclear magnetic resonance and nuclear quadrupole resonance techniques

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CoO_2 is the parent compound for the superconductor $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ and was widely believed to be a Mott insulator. We performed ^{59}Co nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies on Li_xCoO_2 ($x = 0.35, 0.25, 0.12$, and 0.0) to uncover the electronic state and spin correlations in this series of compounds which was recently obtained through electrochemical de-intercalation of Li from pristine LiCoO_2 . We find that although the antiferromagnetic spin correlations systematically increase with decreasing Li-content (x), the end member, CoO_2 is a non-correlated metal that well satisfies the Korringa relation for a Fermi liquid. Thus, CoO_2 is not simply located at the limit of $x \rightarrow 0$ for A_xCoO_2 ($\text{A} = \text{Li}, \text{Na}$) compounds. The disappearance of the electron correlations in CoO_2 is due to the three dimensionality of the compound which is in contrast to the highly two dimensional structure of A_xCoO_2 .

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Electronic correlations and superconductivity in transition-metal oxides have been a main focus in condensed matter physics since the discovery of high transition-temperature (T_c) superconductivity in copper oxides. The hydrated cobalt-oxide superconductor $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ has intensified the research interest in the past few years[1]. This compound bears similarities to the high- T_c copper oxides in that it has a quasi-two dimensional crystal structure and contains a transition-metal element that carries a spin of $\frac{1}{2}$. Indeed, nuclear quadrupole resonance (NQR) measurements on $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ have found T^3 variation below T_c in the spin-lattice relaxation rate $1/T_1$, which is a strong indication of existence of line nodes in the superconducting gap function [2, 3, 4]. Precise measurements of the Knight shift in a high quality single crystal reveals that the spin susceptibility decreases below T_c along both a - and c -axis directions, which indicates that the Cooper pairs are in the spin-singlet state [5]. Thus, the superconductivity in $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ appears to be of d -wave symmetry, as in the case of high- T_c copper oxides. It has also been found that antiferromagnetic spin correlations are present in the superconducting cobaltates, though being much weaker than those in the cuprates [2, 3]. The correlations are anisotropic in the spin space [6], which is different from the cuprate case.

Then, a natural question is how to model the cobalt oxides. Many authors applied the so-called $t-J$ model that had been widely used to describe the cuprates [7, 8, 9]. In these theories, one virtually starts from CoO_2 in which Co is in the Co^{4+} state and there is one electron ($s =$

$1/2$) in the lowest level (a_{1g} orbital). Upon adding Na, one dopes electrons into the a_{1g} orbital, and creates a Co^{3+} ($s = 0$) state. In such a scenario, one may be in a situation of dealing with a doped Mott insulator, as in the cuprates case [7, 8, 10]. Therefore, it is important to synthesize the CoO_2 phase and reveal its electronic ground state. Unfortunately, it has been chemically difficult to obtain pure phase of CoO_2 , or even Na_xCoO_2 with $x \leq 0.25$, though some efforts have been reported [11, 12, 13].

In this paper, we report ^{59}Co NMR and NQR studies to uncover the electronic state and spin correlations in Li-deficient phases, Li_xCoO_2 ($x = 0.35, 0.25$, and 0.12), and the CoO_2 phase. Although the antiferromagnetic spin correlation increases with reducing Li-content (x), the end member, CoO_2 is found to be a non-correlated metal that well satisfies the Korringa relation for a Fermi liquid. The result obtained from our CoO_2 sample is different from the one reported earlier [11] in both the temperature (T) dependence and the magnitude of the $1/T_1$. It turns out that the earlier result correspond to that of our $\text{Li}_{0.12}\text{CoO}_2$. We argue that, however, the disappearance of the electron correlations in pure CoO_2 is due to the three dimensionality of the compound which collapses from the highly two dimensional structure of A_xCoO_2 ($\text{A} = \text{Li}, \text{Na}$) when Li is completely removed. The systematic evolutions of the electron correlations in Li_xCoO_2 ($x = 0.35, 0.25$, and 0.12), as well as in $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ ($x = 0.35, 0.33, 0.28$, and 0.25) [3], are consistent with the theoretical postulation that A_xCoO_2 ($\text{A} = \text{Li}, \text{Na}$) with small x be near a magnetic instability [7, 8].

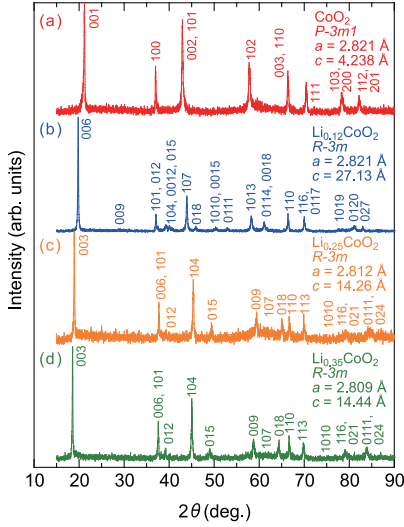


FIG. 1: (Color online) X-ray powder diffraction patterns for (a) CoO₂, (b) Li_{0.12}CoO₂, (c) Li_{0.25}CoO₂, and (d) Li_{0.35}CoO₂ samples. For these samples, Rietveld refinement of the crystal structure was unsuccessful, as the use of an airtight sample holder had significantly deteriorated the resolution of the diffraction patterns.

Polycrystalline samples of Li_xCoO₂ ($x = 0.35, 0.25$, and 0.12) and CoO₂ ($x = 0.0$) were synthesized through electrochemical de-intercalation of Li from pristine LiCoO₂, as described elsewhere [14, 15]. Approximately 100 mg of single-phase LiCoO₂ pellet (without additives) was electrochemically oxidized with a constant current of 0.1 mA in an airtight flat cell filled with a nonaqueous electrolyte. The Li content (or the amount of Li ions to be extracted, i.e. $1-x$) of each sample was precisely controlled by the reaction duration based on Faraday's law. Typically, a 100-mg LiCoO₂ pellet was charged for 178, 205, 241, and 274 h to obtain the $x = 0.35, 0.25, 0.12$, and 0.0 (i.e. CoO₂) phases, respectively. As seen in Fig.1, x-ray powder diffraction analysis evidenced that all the samples are of single phase with characteristic crystal structures typical for their Li compositions. Sharp diffraction peaks throughout the XRD patterns demonstrate that our Li_xCoO₂ and CoO₂ samples are chemically homogenous with good crystallinity. The actual x values determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were in excellent agreement with the theoretical ones, indicating that the full amount of electricity due to the current was used for Li de-intercalation from LiCoO₂. Since high-valent cobalt oxides tend to experience chemical instability when exposed to atmospheric moisture, sample handling and characterization were carefully made in an inert gas atmosphere. A part of the electrochemically-treated samples (~ 70 mg) was encapsulated into a Pyrex ampule filled with Ar gas. NMR/NQR measurements

were performed by using a phase coherent spectrometer. The NQR measurements were performed at zero magnetic field. The NMR and NQR spectra were taken by changing the external magnetic field (H) at a fixed rf frequency of 71.1 MHz and by changing rf frequency and recording the spin echo intensity step by step, respectively. The value of $1/T_1$ was extracted by fitting the nuclear magnetization obtained by recording the spin echo intensity to the Master equation[16, 17].

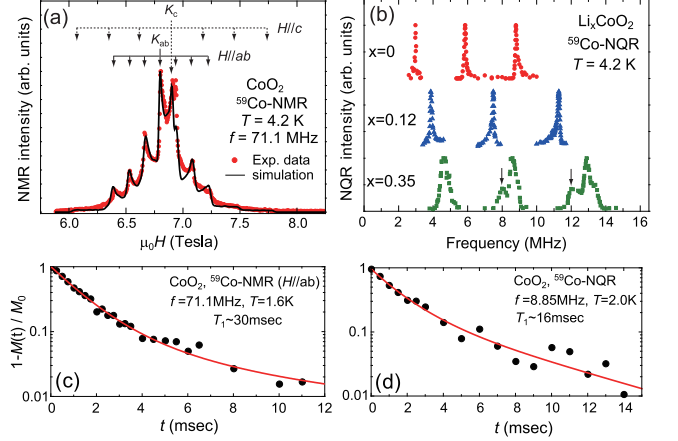


FIG. 2: (Color online) (a) ⁵⁹Co NMR spectra for CoO₂ measured at $T = 4.2$ K. The NMR frequency is 71.1 MHz. Solid and dotted arrows indicate the two sets of seven NMR peaks originated from anisotropy of the Knight shift, respectively. (b) NQR spectrum for Li_xCoO₂ ($x = 0.0, 0.12$, and 0.35) measured at $T = 4.2$ K. Arrows indicate extrinsic NQR peaks occurred due to aging (degradation). (c) and (d) are typical data sets of ⁵⁹Co nuclear recovery curves for CoO₂ obtained by NMR and NQR, respectively (see text).

Figure 2 (a) shows a representative ⁵⁹Co-NMR spectrum for CoO₂. The spectrum shows a typical randomly-oriented powder pattern. Since ⁵⁹Co nucleus has nuclear spin $I = 7/2$, an NMR spectrum has seven peaks due to the quadrupole interaction[18]. As schematically shown by solid and dotted arrows in Fig.2(a), the observed spectrum consists of two central peaks originated from the anisotropy of the Knight shift along the ab - (K_{ab}) and c - (K_c) directions and each central peak is accompanied by six satellite peaks. The numerical calculation considering the quadrupole effect up to the second-order perturbation completely reproduced the experimental result (solid curve in Fig.2 (a)). The clear peak structure attests the high quality of the sample. Thus, we are able to obtain the values of K_{ab} and K_c precisely from the NMR spectra. Figure.2 (b) shows the ⁵⁹Co-NQR spectra for Li_xCoO₂ ($x = 0.0, 0.12$, and 0.35) observed at zero magnetic field. As in Na_xCoO₂·yH₂O[2, 3], three NQR transition lines arising from $I = 7/2$ are clearly observed in Li_xCoO₂. For $x = 0.35$, satellite peaks are observed as indicated by the arrows in Fig.2(b). It indicates

that a secondary phase is present in this composition although X-ray diffraction immediately after sample synthesis showed a single-phase pattern. Since these peaks increase in intensity as time elapsed (not shown), this is an extrinsic phase that arises after the X-ray diffraction analysis.

Figures 2 (c) and (d) show typical datasets of ^{59}Co nuclear recovery curves to obtain T_1 by NMR and NQR, respectively. As drawn in solid curves in figures, they can be fitted by single component of theoretical curves[16, 17], even though the T_1 is measured in powdered sample. Compared to the early report in which the NMR spectrum did not show clear peak structure since it was a superposition of signals from different phases and T_1 is not of single component [11], it is obvious that the present sample has much better quality, and the result represents, we believe, the intrinsic property of CoO_2 .

The NQR parameters are summarized in Table.1. Here ν_Q and asymmetry parameter η are defined as $\nu_Q \equiv \nu_z = \frac{3}{2I(2I-1)\hbar} e^2 Q \frac{\partial^2 V}{\partial z^2}$, $\eta = \frac{|\nu_x - \nu_y|}{\nu_z}$, with Q and $\frac{\partial^2 V}{\partial \alpha^2}$ ($\alpha = x, y, z$) being the nuclear quadrupole moment and the electric field gradient (EFG) at the position of the Co nucleus, respectively.[18] Notably, ν_Q increases with increasing x . This assures electron doping by the increasing of Li-content. On the other hand, η is almost the same in $x = 0.12$ and 0.35 , but is substantially reduced in CoO_2 . This is because the CoO_2 phase crystallizes in a simple structure containing CoO_2 layers only (the so-called O1-type structure), while the crystal of Li_xCoO_2 consists of alternate stacking of Li_x and CoO_2 blocks. [14].

TABLE I: NQR parameters for Li_xCoO_2 obtained at 4.2 K.

sample	$^{59}\nu_Q$ (MHz)	η
CoO_2	2.93	0.05 ± 0.01
$\text{Li}_{0.12}\text{CoO}_2$	3.76	0.09 ± 0.01
$\text{Li}_{0.35}\text{CoO}_2$	4.32	0.10 ± 0.02

Figures 3 (a) shows the T dependence of the Knight shift (K_{ab} and K_c) for three samples with different Li content. As clearly seen in the figure, both K_{ab} and K_c of Li_xCoO_2 do not depend on temperature. Here, the Knight shift consists of contributions from the spin susceptibility, K_s , and from the orbital susceptibility (Van Vleck susceptibility), K_{orb} . $K = K_s + K_{orb}$, with K_{orb} being T -independent but K_s being T -dependent generally. $K_s(T)$ and K_{orb} are respectively related to the spin susceptibility χ_s and orbital susceptibility χ_{orb} as $K_s(T) = A_{hf}\chi_s(T)$ and $K_{orb} = A_{orb}\chi_{orb}$, where A_{hf} is the hyperfine coupling constant between the nuclear and the electron spins. The results show that the spin susceptibility in Li_xCoO_2 is T -independent.

Figure 3 (b) shows the T dependence of $1/T_1T$ measured by ^{59}Co -NMR with $H \parallel ab$. Surprisingly, the $1/T_1T$

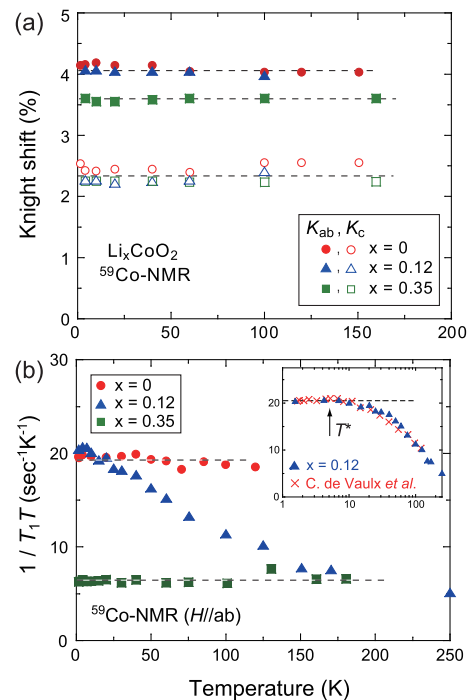


FIG. 3: (Color online) (a) T dependence of the Knight shift (K) for Li_xCoO_2 ($x = 0.35, 0.12$, and 0.0) along ab (solid symbols) and c -axis (open symbols), respectively. Dotted lines indicate the relation of $K = \text{constant}$. (b) T dependence of ^{59}Co -NMR $1/T_1T$ for Li_xCoO_2 ($x = 0.35, 0.12$, and 0.0) measured at the field along the $a(b)$ -axis. Inset shows the semi-log plot of T dependence of ^{59}Co -NMR $1/T_1T$ for $\text{Li}_{0.12}\text{CoO}_2$ ($H \parallel ab$) along with the data referred from Ref. [11]. Dotted lines indicate the relation of $1/T_1T = \text{constant}$. Arrow indicates T^* . (see text)

for CoO_2 is T -independent. Together with the T -independent Knight shift in CoO_2 , the Korringa relation is satisfied as discussed later in more detail. This is a strong and the first evidence for a weakly-correlated ground state of CoO_2 .

De Vaulx *et al* [11] suggested that CoO_2 is a strongly correlated system on the basis of a small value of the characteristic temperature, T^* , below which the Korringa relation holds. However, as seen in Fig.3 (b) inset, we find that their result is almost the same as that for our $\text{Li}_{0.12}\text{CoO}_2$ sample. As the authors acknowledged [11], their sample contained a Li-rich phase as impurity. We suggest that the present results clarify, for the first time, the true electronic state of CoO_2 .

We further measured the T_1 systematically by ^{59}Co -NQR at zero magnetic field, which corresponds to the configuration of $H \parallel c$ -axis since the principal axis of the EFG is along the c -axis. As shown in Fig.4, the T dependence of $1/T_1T$ shows systematic change with decreasing Li-content, except for CoO_2 which will be discussed separately later. With decreasing x from 0.35 to 0.12 , $1/T_1T$ increases with decreasing T , indicating

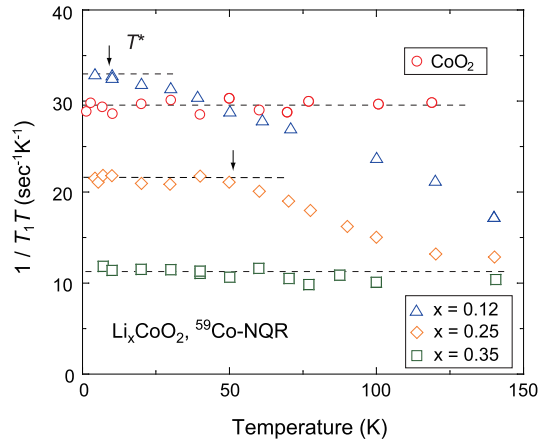


FIG. 4: (Color online) T dependence of ^{59}Co -NQR $1/T_1T$ for Li_xCoO_2 ($x = 0.35, 0.25, 0.12$, and 0.0) Dotted lines and arrows indicate the relation of $1/T_1T = \text{constant}$ and T^* , respectively.

that the electron correlations are induced. Also, the increasing is more pronounced in samples with smaller x , which indicates that the spin correlation is stronger in samples with smaller x . A similar situation was encountered in $\text{Na}_x\text{CoO}_2 \cdot 1.3\text{H}_2\text{O}$ ($x = 0.35, 0.33, 0.28$, and 0.25) [3]. As in that case, the correlation is antiferromagnetic in origin since the Knight shift is T -independent. The $1/T_1T$ becomes constant below T^* , indicating a renormalized Fermi liquid state below T^* . This situation resembles that in electron-doped cuprate $\text{Pr}_{0.91}\text{LaCe}_{0.09}\text{CuO}_4$ where $T^* \sim 60$ K [19]. Furthermore, T^* decreases from 50 K for $x = 0.25$ to 7 K for $x = 0.12$. This also indicates that a sample with smaller x is closer to a magnetic instability. Therefore, the results are consistent with the theories for a compound near a magnetic transition [7, 8].

However, $1/T_1T$ is constant for CoO_2 . This abrupt change in the electronic state is clearly due to the abrupt change in the crystal structure. The Li_xCoO_2 phase with finite x has a highly two-dimensional crystal structure in which the interlayer Co-Co distance ($d_{\text{Co-Co}}$) is as large as 5.0-5.1 Å, while CoO_2 crystallizes in a less anisotropic structure. Since there is no "spacer" layer between two adjacent CoO_2 blocks when Li ions are completely extracted, the $d_{\text{Co-Co}}$ value is reduced to 4.24 Å in CoO_2 . The emergent three dimensionality is believed to be the origin of the weak electron correlation of CoO_2 .

Finally, we examine if there exists any renormalization effect in CoO_2 . To this end, we evaluate the Korringa ratio, $S = T_1TK_s^2 \frac{4\pi k_B}{\hbar} \left(\frac{\gamma_n}{\gamma_e}\right)^2$. This quantity is unity for a free electron system. It is much smaller than the unity for a antiferromagnetically correlated metal but much larger than the unity for a ferromagnetically correlated metal [20]. In the present case, we use the $K_{\text{orb}}^a = 2.96\%$ and

$K_{\text{orb}}^c = 1.72\%$ obtained from recent NMR study in single crystalline $\text{Na}_{0.42}\text{CoO}_2$ [6], then we obtain $S = 1.12 \pm 0.04$ for CoO_2 . Therefore, *CoO₂ is a conventional metal that well conforms to Fermi liquid theory.*

In conclusion, we have presented ^{59}Co -NMR and NQR measurements and analysis on Li_xCoO_2 ($x = 0.0-0.35$). The antiferromagnetic-like spin fluctuations develop when Li is de-intercalated from $\text{Li}_{0.35}\text{CoO}_2$, which is consistent with the picture that the member of the families A_xCoO_2 ($\text{A} = \text{Li}, \text{Na}$) with small x be viewed as a doped spin 1/2 system. Due to the emergent three-dimensionality of the crystal structure, however, CoO_2 , the $x = 0$ end member of A_xCoO_2 , is a conventional metal that well conforms to Fermi liquid theory. The result highlights the importance of two dimensionality for electron correlations in A_xCoO_2 , as was the case that water intercalated into non-correlated $\text{Na}_{0.42}\text{CoO}_2$ brings about spin fluctuations [6]. We hope that these results form a foundation for understanding cobalt oxides and the superconductivity developed out of there.

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